

TITLE
APPARATUS FOR ANALYZING MIXTURES OF GASES

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This application claims the benefit of U.S. Provisional Application No. 457,754, filed March 26, 2003, and U.S. Provisional Application No. 457,761, filed March 26, 2003, each of which is incorporated in
10 its entirety as a part hereof for all purposes.

Field of the Invention

The present invention involves an apparatus for sensing and analyzing various gases, including NO_x,
15 hydrocarbons, carbon monoxide and oxygen, in a multi-component gas system using chemical sensors and chemical sensor arrays. The sensors and sensor arrays use chemo/electro-active materials to detect the presence of, and/or calculate the concentration of,
20 individual gases within the multi-component gas system.

Technical Background

The use of chemical sensing devices to detect
25 certain gases is known. Many attempts have been made to find a material with selectivity and sensitivity for a specific gas. For example, US 4,535,316 discloses a resistive sensor for measuring oxygen. See also H. Meixner et al, *Sensors and Actuators*, B 33 (1996)
30 198-202. It is apparent that different materials must be used for each gas to be detected. However, when a gas is part of a multi-component system, using one material to detect a specific gas is difficult because of the cross-sensitivities of the material to the
35 various component gases of the mixture.

One example of a multi-component gaseous system is a combustion gas emission, which can include

oxygen, carbon monoxide, nitrogen oxides, hydrocarbons, CO₂, H₂S, sulfur dioxide, hydrogen, water vapor, halogens and ammonia. See H. Meixner et al, *Fresenius' J. Anal. Chem.*, 348 (1994) 536-541. In many combustion processes, there is a need to determine whether the gas emissions meet requirements established by federal and state air quality regulations. Several types of gas sensors have been developed to address this need. See, for example, US 5, 630,920, which discloses an electrochemical oxygen sensor; US 4,770,760, which discloses a sensor for detecting oxygen and oxides of nitrogen; and US 4,535,316, which discloses a resistive sensor for measuring oxygen. It would be advantageous to be able to simultaneously analyze two or more components of a mixture such as a combustion gas emission, to calculate concentration for example, in terms only of data generated by direct contact of the gases with a sensor and without having to separate any of the gases in the mixture. Prior art methods do not currently meet this need.

Numerous sensors have also been disclosed to detect gases evolving from foods and for use in other applications involving relatively low temperatures. See K. Albert et al, *Chem. Rev.*, 200 (2000) 2595-2626. Arrays of several undoped and doped tin oxide sensors have also been disclosed for use in detecting various combustion gases up to 450°C [see C. Di Natale et al, *Sensors and Actuators*, B 20 (1994) 217-224; and J. Getino et al, *Sensors and Actuators*, B33 (1996) 128-133]; and the effect of operating temperature on the response of tin oxide bases sensor arrays was studied up to 450°C. See C. Di Natale, *Sensors and Actuators* B23 (1995) 187-191. Higher temperatures, however, and the highly corrosive environment in which chemical sensors would be used to monitor combustion gases, can alter or impair the performance of a sensor array developed for low-temperature applications. High

temperature environments consequently require materials other than those previously known in the art that will be both chemically and thermally stable, and that will maintain measurable responses to the gases of interest,
5 in such demanding conditions.

Addressing this need would permit the use of a chemical sensor to measure combustion emissions, such as automobile exhausts, and determine whether those
10 emissions meet functional and mandated requirements. In addition, it has surprisingly been found that the apparatus of this invention that are useful for analyzing high temperature gases, such as automotive emissions, may be employed with equal effectiveness in
15 analyzing low temperature gases.

Summary of the Invention

This invention provides a method for directly
20 sensing gas components in a multi-component gas system, comprising the steps of: (i) exposing a chemical sensor comprising an array of at least two chemo/electro-active materials to a multi-component gas system, detecting a response, and directly measuring
25 the response of each chemo/electro-active material. Preferably the chemo/electro-active material is a semiconducting material, and the multi-component gas system is a combustion process emission. The response that is measured can be a measurement of capacitance,
30 voltage, current, AC impedance, or DC resistance.

This invention also provides a chemical sensor for directly sensing the presence of gas components in a multi-component gas system, comprising
35 a substrate; an array of at least two chemo/electro-active materials on said substrate; and a means for detecting a response from said chemo/electro-active materials when exposed to said analyte gas component(s)

in the system. Preferably the chemo/electro-active material is a semiconducting material, and the multi-component gas system is a combustion process emission. The response that is detected can be an electrical
5 property such as capacitance, voltage, current, AC impedance, or DC resistance. The device can additionally contain a housing, means for measuring the detected responses, and means for analyzing the results of the measured responses in order to identify the
10 presence and/or concentrations of the analyte gas component(s).

This invention also provides for a chemical sensor device for directly sensing the presence and/or
15 concentration of gas component(s) in a multi-component gas system, comprising: a substrate; an array of at least two chemo/electro-active materials deposited on said substrate; a means for detecting a change in electrical properties of said chemo/electro-active
20 materials upon exposure to said multi-component gas component(s); means for analyzing the results of the detected changes in electrical properties in order to identify the presence and/or concentrations of said gas component(s); and a housing. The chemo/electro-active
25 materials may be semiconducting materials.

Yet another embodiment of this invention is an apparatus for analyzing a multi-component gas mixture including (a) an array of at least three chemo/electro-
30 active materials, each chemo/electro-active material exhibiting a different electrical response characteristic, upon exposure to the gas mixture, than each of the other chemo/electro-active materials; (b) means for determining an electrical response of each
35 chemo/electro-active material upon exposure of the array to the gas mixture; and (c) means for (i) detecting the presence of a subgroup of gases in the mixture from the responses of a first group of at least

two chemo/electro-active materials, and (ii) detecting the presence of an individual component gas in the mixture from the responses of a second group of at least two chemo/electro-active materials.

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Yet another embodiment of this invention is an apparatus for analyzing a multi-component gas mixture that includes:

(a) an array of two or more chemo/electro-active materials, each chemo/electro-active material exhibiting a different electrical response characteristic, upon exposure at a selected temperature to the gas mixture, than each of the other chemo/electro-active materials;

15 wherein the chemo/electro-active materials are selected from any one or more members of the group consisting of (i) the chemo/electro-active materials that comprise M^1O_x , (ii) the chemo/electro-active materials that comprise $M^1_aM^2_bO_x$, and (iii) the chemo/electro-active materials that comprise $M^1_aM^2_bM^3_cO_x$;

20 wherein M^1 is selected from the group consisting of Al, Ce, Cr, Cu, Fe, Ga, Mn, Nb, Nd, Ni, Pr, Sb, Sn, Ta, Ti, W and Zn;

25 wherein M^2 and M^3 are each independently selected from the group consisting of Ga, La, Mn, Ni, Sn, Sr, Ti, W, Y, Zn;

30 wherein M^1 and M^2 are each different in $M^1_aM^2_bO_x$, and M^1 , M^2 and M^3 are each different in $M^1_aM^2_bM^3_cO_x$;

wherein a, b and c are each independently about 0.0005 to about 1; and

35 wherein x is a number sufficient so that the oxygen present balances the charges of the other elements in the chemo/electro-active material; and

(b) means for determining an electrical response of each chemo/electro-active material upon exposure of the array to the gas mixture.

5 In various particularized embodiments, the apparatus may further include, if desired, a heater to continually maintain the chemo/electro-active materials at a minimum temperature of about 500°C or above; and

10 means for obtaining, from no information about the gas mixture other than the individual electrical response of the chemo/electro-active materials, a determination related to the presence or concentration of a component in the gas mixture.

15 This invention also provides a method of analyzing a gas, such as determining information related to the presence in, or relative concentration of, one or more components in a gas mixture; or a
20 method of controlling the process or operation of a device by providing and/or using an apparatus of this invention.

25 Description of the Drawings

 Figure 1 depicts an array of chemo/electro-active materials.

 Figure 2 is a schematic of the pattern of
30 interdigitated electrodes overlaid with a dielectric overlayer, forming sixteen blank wells, in an array of chemo/electro-active materials.

 Figure 3 depicts the electrode pattern,
35 dielectric pattern, and sensor material pattern in an array of chemo/electro-active materials.

Figure 4 is a plot of the results of a test run in which the concentration of NOx was determined by an apparatus of the invention.

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Detailed Description of the Invention

The present invention is a method and apparatus for directly sensing one or more analyte gases in a multi-component gas system under variable
10 temperature conditions. By "directly sensing" is meant that an array of gas-sensing materials will be exposed to a mixture of gases that constitutes a multi-component gas system, such as in a stream of flowing gases. The array may be situated within the gas
15 mixture, and more particularly within the source of the gas mixture, if desired. Alternatively, the array may reside in a chamber to which the gas mixture is directed from its source at another location. When gas is directed to a chamber in which an array is located,
20 the gas mixture may be inserted in and removed from the chamber by piping, conduits or any other suitable gas transmission equipment.

A response may be obtained upon exposure of
25 the gas-sensing materials to the multi-component gas mixture, and the response will be a function of the concentrations of one or more of the analyte gases themselves in the gas mixture. The sensor materials will be exposed simultaneously (or substantially
30 simultaneously) to each of the analyte gases, and an analyte gas does not have to be physically separated from the multi-component gas mixture to be able to conduct an analysis of the mixture and/or one or more analyte components thereof. This invention can be
35 used, for example, to obtain responses to, and thus to detect and/or measure the concentrations, of combustion gases, such as oxygen, carbon monoxide, nitrogen oxides, hydrocarbons such as butane, CO₂, H₂S, sulfur

dioxide, halogens, hydrogen, water vapor, an organo-phosphorus gas, and ammonia, at variable temperatures in gas mixtures such as automobile emissions.

5 This invention utilizes an array of sensing materials to analyze a gas mixture and/or the components thereof to, for example, obtain a response to, detect the presence of and/or calculate the concentration of one or more individual analyte gas
10 components in the system. By "array" is meant at least two different materials that are spatially separated, as shown for example in Fig. 1. The array may contain, for example, 3, 4, 5, 6, 8, 10 or 12 gas-sensing materials, or other greater or lesser numbers as
15 desired. It is preferred that there be provided at least one sensor material for each of the individual gases or subgroups of gases in the mixture to be analyzed. It may be desirable, however, to provide more than one sensor material that is responsive to an
20 individual gas component and/or a particular subgroup of gases in the mixture. For example, a group of at least 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 or 12 sensors could be used to detect the presence of, and/or calculate the concentration of, one or more individual
25 component gases and/or one or more subgroups of gases in the mixture. Groups of sensors, which may or may not have members in common, could be used to obtain a response to an analyte that is an individual gas component or a subgroup of gases in the mixture. A
30 subgroup of gases that is, as the subgroup, an analyte may or may not contain as a member an individual gas that is itself also an analyte.

 This invention is useful for detecting those
35 gases that are expected to be present in a gas stream. For example, in a combustion process, gases that are expected to be present include oxygen, nitrogen oxides (such as NO, NO₂, N₂O or N₂O₄), carbon monoxide,

hydrocarbons (such as C_nH_{2n+2} , and as same may be saturated or unsaturated, or be optionally substituted with hetero atoms; and cyclic and aromatic analogs thereof), ammonia or hydrogen sulfide, sulfur dioxide, CO₂, or methanol. Other gases of interest may include alcohol vapors, solvent vapors, hydrogen, water vapor, and those deriving from saturated and unsaturated hydrocarbons, ethers, ketones, aldehydes, carbonyls, biomolecules and microorganisms. The component of a multi-component gas mixture that is an analyte of interest may be an individual gas such as carbon monoxide; may be a subgroup of some but not all of the gases contained in the mixture, such as the nitrogen oxides (NO_x) or hydrocarbons; or may be a combination of one or more individual gases and one or more subgroups. When a subgroup of gases is an analyte, a chemo/electro-active material will respond to the collective concentration within a multi-component gas mixture of the members of the subgroup together.

The analyte gas(es) contained in the mixture to which the chemo/electro-active material will be exposed can be a single gas, a subgroup of gases together, or one or more gases or subgroups mixed with an inert gas such as nitrogen. Particular gases of interest are donor and acceptor gases. These are gases that either donate electrons to the semiconducting material, such as carbon monoxide, H₂S and hydrocarbons, or accept electrons from the semiconducting material, such as O₂, nitrogen oxides (commonly depicted as NO_x), and halogens. When exposed to a donor gas, an n-type semiconducting material will have a decrease in electrical resistance, increasing the current, and it, therefore, will show an increase in temperature due to I^2R heating. When exposed to an acceptor gas, an n-type semiconducting material will have an increase in electrical resistance, decreasing the current, and therefore will show a decrease in

temperature due to I^2R heating. The opposite occurs in each instance with p-type semiconducting materials.

Obtaining information related to the
5 compositional content of a gas mixture using these
sensor materials, such as measurement of gas
concentrations, can be based on a change in an
electrical property, such as AC impedance, of at least
one, but preferably each and all, of the materials upon
10 exposure of the materials to a mixture containing one
or more analyte gases. Analysis of a gas mixture can
also be performed in terms of extent of change in other
electrical properties of the sensor materials, such as
capacitance, voltage, current or AC or DC resistance.
15 Change in DC resistance may be determined, for example,
by measuring change in temperature at constant voltage.
The change in one of these illustrative properties of a
sensor material is a function of the partial pressure
of an analyte gas within the gas mixture, which in turn
20 determines the concentration at which the molecules of
the analyte gases become adsorbed on the surface of a
sensor material, thus affecting the electrical response
characteristics of that material. By using an array of
chemo/electro-active materials, a pattern of the
25 respective responses exhibited by the materials upon
exposure to a mixture containing one or more analyte
gases can be used to simultaneously and directly detect
the presence of, and/or measure the concentration of,
at least one gas in a multi-component gas system. The
30 invention, in turn, can be used to determine the
composition of the gas system. The concept is
illustrated schematically in Figure 1 and is
exemplified below.

35 To illustrate, consider the theoretical
example below of the exposure of a sensor material to a
mixture containing an analyte gas. Where a response
is obtained, the event is depicted as positive (+), and

where no response is obtained, the event is depicted as negative (-). Material 1 responds to Gas 1 and Gas 2, but shows no response to Gas 3. Material 2 responds to Gas 1 and Gas 3, but shows no response to Gas 2, and
5 Material 3 responds to Gas 2 and Gas 3, but shows no response to Gas 1.

	Material 1	Material 2	Material 3
Gas 1	+	+	-
Gas 2	+	-	+
Gas 3	-	+	+

10 Therefore, if an array consisting of Materials 1, 2 and 3 gives the following response to an unknown gas,

	Material 1	Material 2	Material 3
Unknown Gas	+	-	+

15 then the unknown gas would be identified as Gas 2. The response of each sensor material would be a function of the partial pressure within the mixture of, and thus the concentration of, an analyte gas or the collective concentration of a subgroup of analyte gases; and the
20 response could be quantified or recorded as a processible value, such as a numerical value. In such case, the values of one or more responses can be used to generate quantitative information about the presence within the mixture of one or more analyte gases. In a
25 multicomponent gas system, chemometrics, neural networks or other pattern recognition techniques could be used to calculate the concentration of one or more analyte gases in the mixture of the system.

30 The sensing materials used are chemo/electro-active materials. A "chemo/electro-active material" is

a material that has an electrical response to at least one individual gas in a mixture. Some metal oxide semiconducting materials, mixtures thereof, or mixtures of metal oxide semiconductors with other inorganic compounds are chemo/electro-active, and are particularly useful in this invention. Each of the various chemo/electro-active materials used herein preferably exhibits an electrically-detectable response of a different kind and/or extent, upon exposure to the mixture and/or an analyte gas, than each of the other chemo/electro-active materials. As a result, an array of appropriately chosen chemo/electro-active materials can be used to analyze a multi-component gas mixture, such as by interacting with an analyte gas, sensing an analyte gas, or determining the presence and/or concentration of one or more analyte gases or subgroups in a mixture, despite the presence therein of interfering gases that are not of interest. Preferably the mole percentages of the major components of each gas-sensing material differs from that of each of the others.

The chemo/electro-active material can be of any type, but especially useful are semiconducting metal oxides such as SnO_2 , TiO_2 , WO_3 and ZnO . These particular materials are advantageous due to their chemical and thermal stability. The chemo/electro-active material can be a mixture of two or more semiconducting materials, or a mixture of a semiconducting material with an inorganic material, or combinations thereof. The semiconducting materials of interest can be deposited on a suitable solid substrate that is an insulator such as, but not limited to, alumina or silica and is stable under the conditions of the multi-component gas mixture. The array then takes the form of the sensor materials as deposited on the substrate. Other suitable sensor materials include single crystal or polycrystalline semiconductors of the

bulk or thin film type, amorphous semiconducting materials, and semiconductor materials that are not composed of metal oxides. In a preferred embodiment, the substrate is not zirconia.

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In various embodiments, the substrate may be a high-temperature multilayer ceramic, which is prepared from Al_2O_3 , AlN , and, to a smaller extent, BeO and SiC . The alumina content is dominant, however, with about 92 - 96 weight% of the composition being Al_2O_3 . The structure consists of many layers of ceramic, with metallization between the layers, and via holes through the layers for electrical contact. A well known application of large modules with many layers of ceramic is IBM's pioneering product "Thermal Conduction Module" (TCM) for mainframe computers in 1983. The module had 33 layers, and 133 silicon chips were mounted by flip chip soldering.

20 This type of non-sintered, pliable ceramic consists of alumina powder, organic binders and solvents. The material is spread from a container down on a transport carrier underneath. The ceramic "tape" ("green sheet") is given the appropriate thickness on the transport carrier by passing underneath a "doctor blade" in a precisely controlled distance. The tape is cut to correct size, and holes and component cavities are punched out with a numerically controlled punching tool, or with a permanent, product specific punching tool for high production volume of a given product. Metallization of the via holes and fabrication of conductors is done by screen printing of tungsten (or molybdenum). These are the only metals that can withstand the high process temperature during the subsequent sintering process. All layers are laminated together under hydrostatic (or uni-axial) pressure at elevated temperature (500 - 600°C) to evaporate the binder and solvent. Then the

whole structure is sintered at 1370 - 1650°C, 30 - 50 hours, in a hydrogen atmosphere.

For small circuits, many modules are made on one substrate, and the individual circuits can be parted by breaking the substrate at the end of the process. Then the external contacts are brazed to the substrate, and finally gold may be plated on the surface with nickel as a diffusion barrier on top of the tungsten. The plating is preferably done electrolytically to achieve sufficient thickness and good conductivity if an electrical contact to all parts of the conductor pattern can be made. Otherwise, chemical plating is used.

During the process, the ceramic shrinks approximately 18% linearly. This is taken into consideration during the design of the circuit, both sideways and in thickness, which affects the characteristic impedance. As the shrinkage is material and process dependent, the finished circuits typically have linear dimensional tolerances 0.5 - 1%. These ceramic substrates have low TCE, a good thermal match to Si and GaAs as well as to leadless SMD components, good control over characteristic impedance, and good high frequency properties. Many layers are possible with high production yield because each layer can be inspected before the lamination, and faulty layers can be discarded. Among the disadvantages are low electrical conductivity in the inner layers (sheet resistivity ~ 15 mohm/sq), and high dielectric constant, which gives delay, inferior pulse rise time and increased power loss and cross talk at very high frequencies.

The chemo/electro-active materials that contain more than one metal do not have to be a compound or solid solution, but can be a multi-phase

physical mixture of discrete metals and/or metal oxides. As there will be varying degrees of solid state diffusion by the precursor materials from which the chemo/electro-active materials are formed, the
5 final materials may exhibit composition gradients, and they can be crystalline or amorphous. Suitable metal oxides are those that

- i) when at a temperature of about 400°C or above, have a resistivity of about 1 to about 10⁶
10 ohm-cm, preferably about 1 to about 10⁵ ohm-cm, and more preferably about 10 to about 10⁴ ohm-cm;
- ii) show a chemo/electro response to at least one gas of interest; and
- iii) are stable and have mechanical
15 integrity, that is are able to adhere to the substrate and not degrade at the operating temperature.

The metal oxides may also contain minor or trace amounts of hydration and elements present in the
20 precursor materials.

The sensor materials may optionally contain one or more additives to promote adhesion to a substrate, or that alter the conductance, resistance or
25 selectivity of the sensor material. Examples of additives to alter the conductance, resistance or selectivity of the sensor material include Ag, Au or Pt, as well as frits. Examples of additives to promote adhesion include frits, which are finely ground
30 inorganic minerals that are transformed into glass or enamel on heating, or a rapidly quenched glass that retains its amorphous quality in the solid state. Frit precursor compounds are melted at high temperature and quenched, usually by rapidly pouring the melt into
35 a fluid such as water, or by pouring through spinning metal rollers. The precursor compounds usually are a mechanical mixture of solid compounds such as oxides, nitrates or carbonates, or can be co-precipitated or

gelled from a solution. Suitable precursor materials for frits include alkali and alkaline earth aluminosilicates and aluminoborosilicates, copper, lead, phosphorus, titanium, zinc and zirconium. Frits as
5 additives may be used in amounts of up to 30 volume percent, and preferably up to 10 volume percent, of the total volume of the chemo/electro-active material from which the sensor is made.

10 If desired, the sensor materials may also contain additives that, for example, catalyze the oxidation of a gas of interest or promote the selectivity for a particular analyte gas; or contain one or more dopants that convert an n semiconductor to
15 a p semiconductor, or vice versa. These additives may be used in amounts of up to 30 weight percent, and preferably up to 10 weight percent, of the chemo/electro-active material from which the sensor is made.

20 Any frits or other additives used need not be uniformly or homogeneously distributed throughout the sensor material as fabricated, but may be localized on or near a particular surface thereof as desired. Each
25 chemo/electro-active material may, if desired, be covered with a porous dielectric overlayer.

The chemo/electro-active materials used as sensor materials in this invention may, for example, be
30 metal oxides of the formula M^1O_x , $M^1_aM^2_bO_x$, or $M^1_aM^2_bM^3_cO_x$; or mixtures thereof, wherein

M^1 , M^2 and M^3 are metals that form stable oxides when fired in the presence of oxygen above 500°C;

35 M^1 is selected from Periodic Groups 2-15 and the lanthanide group;

M^2 and M^3 are each independently selected from Periodic Groups 1-15 and the lanthanide group;

5 M^1 and M^2 are not the same in $M^1_a M^2_b O_x$, and M^1 , M^2 and M^3 are not the same in $M^1_a M^2_b M^3_c O_x$;

a, b, and c are each independently in the range of about 0.0005 to about 1; and

x is a number sufficient so that the oxygen present balances the charges of the other elements present in the chemo/electro-active material.

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In certain preferred embodiments, the metal oxide materials may include those in which

M^1 is selected from the group consisting of
15 Ce, Co, Cu, Fe, Ga, Nb, Nd, Ni, Pr, Ru, Sn, Ti, Tm, W, Yb, Zn, and Zr; and/or

M^2 and M^3 are each independently selected from the group consisting of Al, Ba, Bi, Ca, Cd, Ce, Co, Cr, Cu, Fe, Ga, Ge, In, K, La, Mg, Mn, Mo, Na, Nb, Ni, Pb, Pr, Rb, Ru, Sb, Sc, Si, Sn, Sr, Ta, Ti, Tm, V, W, Y, Yb, Zn, and Zr;

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but in which M^1 and M^2 are not the same in $M^1_a M^2_b O_x$, and M^1 , M^2 and M^3 are not the same in $M^1_a M^2_b M^3_c O_x$.

25 In certain other preferred embodiments, the metal oxide materials may include those in which

$M^1 O_x$ is CeO_x , CoO_x , CuO_x , FeO_x , GaO_x , NbO_x , NiO_x , PrO_x , RuO_x , SnO_x , TaO_x , TiO_x , TmO_x , WO_x , YbO_x , ZnO_x , ZrO_x , SnO_x with Ag additive, ZnO_x with Ag additive, TiO_x with Pt additive, ZnO_x with frit additive, NiO_x with frit additive, SnO_x with frit additive, or WO_x with frit additive; and/or

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$M^1_a M^2_b O_x$ is $Al_a Cr_b O_x$, $Al_a Fe_b O_x$, $Al_a Mg_b O_x$, $Al_a Ni_b O_x$, $Al_a Ti_b O_x$, $Al_a V_b O_x$, $Ba_a Cu_b O_x$, $Ba_a Sn_b O_x$, $Ba_a Zn_b O_x$, $Bi_a Ru_b O_x$, $Bi_a Sn_b O_x$, $Bi_a Zn_b O_x$, $Ca_a Sn_b O_x$, $Ca_a Zn_b O_x$, $Cd_a Sn_b O_x$, $Cd_a Zn_b O_x$, $Ce_a Fe_b O_x$, $Ce_a Nb_b O_x$, $Ce_a Ti_b O_x$, $Ce_a V_b O_x$, $Co_a Cu_b O_x$, $Co_a Ge_b O_x$, $Co_a La_b O_x$, $Co_a Mg_b O_x$, $Co_a Nb_b O_x$, $Co_a Pb_b O_x$, $Co_a Sn_b O_x$, $Co_a V_b O_x$,

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$\text{Co}_a\text{W}_b\text{O}_x$, $\text{Co}_a\text{Zn}_b\text{O}_x$, $\text{Cr}_a\text{Cu}_b\text{O}_x$, $\text{Cr}_a\text{La}_b\text{O}_x$, $\text{Cr}_a\text{Mn}_b\text{O}_x$,
 $\text{Cr}_a\text{Ni}_b\text{O}_x$, $\text{Cr}_a\text{Si}_b\text{O}_x$, $\text{Cr}_a\text{Ti}_b\text{O}_x$, $\text{Cr}_a\text{Y}_b\text{O}_x$, $\text{Cr}_a\text{Zn}_b\text{O}_x$,
 $\text{Cu}_a\text{Fe}_b\text{O}_x$, $\text{Cu}_a\text{Ga}_b\text{O}_x$, $\text{Cu}_a\text{La}_b\text{O}_x$, $\text{Cu}_a\text{Nb}_b\text{O}_x$, $\text{Cu}_a\text{Ni}_b\text{O}_x$,
 $\text{Cu}_a\text{Pb}_b\text{O}_x$, $\text{Cu}_a\text{Sn}_b\text{O}_x$, $\text{Cu}_a\text{Sr}_b\text{O}_x$, $\text{Cu}_a\text{Ti}_b\text{O}_x$, $\text{Cu}_a\text{Zn}_b\text{O}_x$,
5 $\text{Cu}_a\text{Zr}_b\text{O}_x$, $\text{Fe}_a\text{Ga}_b\text{O}_x$, $\text{Fe}_a\text{La}_b\text{O}_x$, $\text{Fe}_a\text{Mo}_b\text{O}_x$, $\text{Fe}_a\text{Nb}_b\text{O}_x$,
 $\text{Fe}_a\text{Ni}_b\text{O}_x$, $\text{Fe}_a\text{Sn}_b\text{O}_x$, $\text{Fe}_a\text{Ti}_b\text{O}_x$, $\text{Fe}_a\text{W}_b\text{O}_x$, $\text{Fe}_a\text{Zn}_b\text{O}_x$,
 $\text{Fe}_a\text{Zr}_b\text{O}_x$, $\text{Ga}_a\text{La}_b\text{O}_x$, $\text{Ga}_a\text{Sn}_b\text{O}_x$, $\text{Ge}_a\text{Nb}_b\text{O}_x$, $\text{Ge}_a\text{Ti}_b\text{O}_x$,
 $\text{In}_a\text{Sn}_b\text{O}_x$, $\text{K}_a\text{Nb}_b\text{O}_x$, $\text{Mn}_a\text{Nb}_b\text{O}_x$, $\text{Mn}_a\text{Sn}_b\text{O}_x$, $\text{Mn}_a\text{Ti}_b\text{O}_x$,
 $\text{Mn}_a\text{Y}_b\text{O}_x$, $\text{Mn}_a\text{Zn}_b\text{O}_x$, $\text{Mo}_a\text{Pb}_b\text{O}_x$, $\text{Mo}_a\text{Rb}_b\text{O}_x$, $\text{Mo}_a\text{Sn}_b\text{O}_x$,
10 $\text{Mo}_a\text{Ti}_b\text{O}_x$, $\text{Mo}_a\text{Zn}_b\text{O}_x$, $\text{Nb}_a\text{Ni}_b\text{O}_x$, $\text{Nb}_a\text{Ni}_b\text{O}_x$, $\text{Nb}_a\text{Sr}_b\text{O}_x$,
 $\text{Nb}_a\text{Ti}_b\text{O}_x$, $\text{Nb}_a\text{W}_b\text{O}_x$, $\text{Nb}_a\text{Zr}_b\text{O}_x$, $\text{Ni}_a\text{Si}_b\text{O}_x$, $\text{Ni}_a\text{Sn}_b\text{O}_x$,
 $\text{Ni}_a\text{Y}_b\text{O}_x$, $\text{Ni}_a\text{Zn}_b\text{O}_x$, $\text{Ni}_a\text{Zr}_b\text{O}_x$, $\text{Pb}_a\text{Sn}_b\text{O}_x$, $\text{Pb}_a\text{Zn}_b\text{O}_x$,
 $\text{Rb}_a\text{W}_b\text{O}_x$, $\text{Ru}_a\text{Sn}_b\text{O}_x$, $\text{Ru}_a\text{W}_b\text{O}_x$, $\text{Ru}_a\text{Zn}_b\text{O}_x$, $\text{Sb}_a\text{Sn}_b\text{O}_x$,
 $\text{Sb}_a\text{Zn}_b\text{O}_x$, $\text{Sc}_a\text{Zr}_b\text{O}_x$, $\text{Si}_a\text{Sn}_b\text{O}_x$, $\text{Si}_a\text{Ti}_b\text{O}_x$, $\text{Si}_a\text{W}_b\text{O}_x$,
15 $\text{Si}_a\text{Zn}_b\text{O}_x$, $\text{Sn}_a\text{Ta}_b\text{O}_x$, $\text{Sn}_a\text{Ti}_b\text{O}_x$, $\text{Sn}_a\text{W}_b\text{O}_x$, $\text{Sn}_a\text{Zn}_b\text{O}_x$,
 $\text{Sn}_a\text{Zr}_b\text{O}_x$, $\text{Sr}_a\text{Ti}_b\text{O}_x$, $\text{Ta}_a\text{Ti}_b\text{O}_x$, $\text{Ta}_a\text{Zn}_b\text{O}_x$, $\text{Ta}_a\text{Zr}_b\text{O}_x$,
 $\text{Ti}_a\text{V}_b\text{O}_x$, $\text{Ti}_a\text{W}_b\text{O}_x$, $\text{Ti}_a\text{Zn}_b\text{O}_x$, $\text{Ti}_a\text{Zr}_b\text{O}_x$, $\text{V}_a\text{Zn}_b\text{O}_x$, $\text{V}_a\text{Zr}_b\text{O}_x$,
 $\text{W}_a\text{Zn}_b\text{O}_x$, $\text{W}_a\text{Zr}_b\text{O}_x$, $\text{Y}_a\text{Zr}_b\text{O}_x$, $\text{Zn}_a\text{Zr}_b\text{O}_x$, $\text{Al}_a\text{Ni}_b\text{O}_x$ with frit
additive, $\text{Cr}_a\text{Ti}_b\text{O}_x$ with frit additive, $\text{Fe}_a\text{La}_b\text{O}_x$ with
20 frit additive, $\text{Fe}_a\text{Ni}_b\text{O}_x$ with frit additive, $\text{Fe}_a\text{Ti}_b\text{O}_x$
with frit additive, $\text{Nb}_a\text{Ti}_b\text{O}_x$ with frit additive,
 $\text{Nb}_a\text{W}_b\text{O}_x$ with frit additive, $\text{Ni}_a\text{Zn}_b\text{O}_x$ with frit
additive, $\text{Ni}_a\text{Zr}_b\text{O}_x$ with frit additive, $\text{Sb}_a\text{Sn}_b\text{O}_x$ with
frit additive, $\text{Ta}_a\text{Ti}_b\text{O}_x$ with frit additive, or $\text{Ti}_a\text{Zn}_b\text{O}_x$
25 with frit additive; and/or
 $\text{M}^1_a\text{M}^2_b\text{M}^3_c\text{O}_x$ is $\text{Al}_a\text{Mg}_b\text{Zn}_c\text{O}_x$, $\text{Al}_a\text{Si}_b\text{V}_c\text{O}_x$,
 $\text{Ba}_a\text{Cu}_b\text{Ti}_c\text{O}_x$, $\text{Ca}_a\text{Ce}_b\text{Zr}_c\text{O}_x$, $\text{Co}_a\text{Ni}_b\text{Ti}_c\text{O}_x$, $\text{Co}_a\text{Ni}_b\text{Zr}_c\text{O}_x$,
 $\text{Co}_a\text{Pb}_b\text{Sn}_c\text{O}_x$, $\text{Co}_a\text{Pb}_b\text{Zn}_c\text{O}_x$, $\text{Cr}_a\text{Sr}_b\text{Ti}_c\text{O}_x$, $\text{Cu}_a\text{Fe}_b\text{Mn}_c\text{O}_x$,
 $\text{Cu}_a\text{La}_b\text{Sr}_c\text{O}_x$, $\text{Fe}_a\text{Nb}_b\text{Ti}_c\text{O}_x$, $\text{Fe}_a\text{Pb}_b\text{Zn}_c\text{O}_x$, $\text{Fe}_a\text{Sr}_b\text{Ti}_c\text{O}_x$,
30 $\text{Fe}_a\text{Ta}_b\text{Ti}_c\text{O}_x$, $\text{Fe}_a\text{W}_b\text{Zr}_c\text{O}_x$, $\text{Ga}_a\text{Ti}_b\text{Zn}_c\text{O}_x$, $\text{La}_a\text{Mn}_b\text{Na}_c\text{O}_x$,
 $\text{La}_a\text{Mn}_b\text{Sr}_c\text{O}_x$, $\text{Mn}_a\text{Sr}_b\text{Ti}_c\text{O}_x$, $\text{Mo}_a\text{Pb}_b\text{Zn}_c\text{O}_x$, $\text{Nb}_a\text{Sr}_b\text{Ti}_c\text{O}_x$,
 $\text{Nb}_a\text{Sr}_b\text{W}_c\text{O}_x$, $\text{Nb}_a\text{Ti}_b\text{Zn}_c\text{O}_x$, $\text{Ni}_a\text{Sr}_b\text{Ti}_c\text{O}_x$, $\text{Sn}_a\text{W}_b\text{Zn}_c\text{O}_x$,
 $\text{Sr}_a\text{Ti}_b\text{V}_c\text{O}_x$, $\text{Sr}_a\text{Ti}_b\text{Zn}_c\text{O}_x$, or $\text{Ti}_a\text{W}_b\text{Zr}_c\text{O}_x$.

35 In certain other preferred embodiments, the
metal oxide materials may include those that are in an
array of first and second chemo/electro-active
materials, wherein the chemo/electro-active materials
are selected from the pairings in the group consisting
40 of

(i) the first material is M^1O_x , and the second material is $M^1_aM^2_bO_x$;

(ii) the first material is M^1O_x , and the second material is $M^1_aM^2_bM^3_cO_x$;

5 (iii) the first material is $M^1_aM^2_bO_x$, and the second material is $M^1_aM^2_bM^3_cO_x$;

(iv) the first material is a first M^1O_x , and the second material is a second M^1O_x ;

(v) the first material is a first $M^1_aM^2_bO_x$, and
10 the second material is a second $M^1_aM^2_bO_x$; and

(vi) the first material is a first $M^1_aM^2_bM^3_cO_x$, and the second material is a second $M^1_aM^2_bM^3_cO_x$;

wherein

M^1 is selected from the group consisting of Ce,
15 Co, Cu, Fe, Ga, Nb, Nd, Ni, Pr, Ru, Sn, Ti, Tm, W, Yb, Zn, and Zr;

M^2 and M^3 are each independently selected from the group consisting of Al, Ba, Bi, Ca, Cd, Ce, Co, Cr, Cu, Fe, Ga, Ge, In, K, La, Mg, Mn, Mo, Na, Nb, Ni, Pb, Pr, Rb, Ru, Sb, Sc, Si, Sn, Sr, Ta, Ti, Tm, V, W, Y, Yb, Zn, and Zr;

but M^1 and M^2 are not the same in $M^1_aM^2_bO_x$, and M^1 , M^2 and M^3 are not the same in $M^1_aM^2_bM^3_cO_x$;

a, b and c are each independently about 0.0005 to
25 about 1; and

x is a number sufficient so that the oxygen present balances the charges of the other elements present in the chemo/electro-active material.

30 In certain other preferred embodiments, an array of two or more chemo/electro-active materials may be selected from the group consisting of (i) the chemo/electro-active materials that include M^1O_x , (ii) the chemo/electro-active materials that include
35 $M^1_aM^2_bO_x$, and (iii) the chemo/electro-active materials that include $M^1_aM^2_bM^3_cO_x$;

wherein M^1 is selected from the group consisting of Al, Ce, Cr, Cu, Fe, Ga, Mn, Nb, Nd, Ni, Pr, Sb, Sn, Ta, Ti, W and Zn;

5 wherein M^2 and M^3 are each independently selected from the group consisting of Ga, La, Mn, Ni, Sn, Sr, Ti, W, Y, Zn;

wherein M^1 and M^2 are each different in $M^1_a M^2_b O_x$, and M^1 , M^2 and M^3 are each different in $M^1_a M^2_b M^3_c O_x$;

10 wherein a, b and c are each independently about 0.0005 to about 1; and

wherein x is a number sufficient so that the oxygen present balances the charges of the other elements in the chemo/electro-active
15 material.

M^1 may for example be selected from the group consisting of Al, Cr, Fe, Ga, Mn, Nb, Nd, Ni, Sb, Sn, Ta, Ti and Zn, or from the group consisting of Ga, Nb, Ni, Sb, Sn, Ta, Ti and Zn. M^2 , M^3 , or M^2 and M^3 may be
20 selected from the group consisting of La, Ni, Sn, Ti and Zn, or the group consisting of Sn, Ti and Zn.

The array may contain other numbers of
25 chemo/electro-active materials such as four, five, six, seven or eight, each of which may for example be a chemo/electro-active material that comprises $M^1_a M^2_b O_x$ as described above. In other embodiments, however, the array may have groupings of other kinds of
30 materials such as the following:

(a) when the array contains 4, 5, 6, 7 or 8 or more chemo/electro-active materials, the chemo/electro-active materials may be selected from the group
35 consisting of (i) at least one chemo/electro-active material that comprises $M^1 O_x$, and (ii) at least 3, 4, 5, 6 or 7 or more chemo/electro-active materials each of which comprises $M^1_a M^2_b O_x$;

- (b) when the array contains 4, 5, 6, 7 or 8 or more chemo/electro-active materials, the chemo/electro-active materials may be selected from the group
- 5 consisting of (i) at least two chemo/electro-active materials each of which comprises M^1O_x , and (ii) at least 2, 3, 4, 5 or 6 or more chemo/electro-active materials each of which comprises $M^1_aM^2_bO_x$;
- 10 (c) when the array contains 4, 5, 6, 7 or 8 or more chemo/electro-active materials, the chemo/electro-active materials may be selected from the group consisting of (i) at least one chemo/electro-active material that comprises M^1O_x , (ii) at least 2, 3, 4, 5
- 15 or 6 or more chemo/electro-active materials each of which comprises $M^1_aM^2_bO_x$, and (iii) at least one chemo/electro-active material that comprises $M^1_aM^2_bM^3_cO_x$;
- 20 (d) when the array contains 4, 5, 6, 7 or 8 or more chemo/electro-active materials, the chemo/electro-active materials may be selected from the group consisting of (i) at least two chemo/electro-active material that comprises M^1O_x , (ii) at least 1, 2, 3, 4
- 25 or 5 or more chemo/electro-active materials each of which comprises $M^1_aM^2_bO_x$, and (iii) at least one chemo/electro-active material that comprises $M^1_aM^2_bM^3_cO_x$; or
- 30 (e) when the array contains 4, 5, 6, 7 or 8 or more chemo/electro-active materials, the chemo/electro-active materials may be selected from the group consisting of (i) at least three chemo/electro-active materials each of which comprises $M^1_aM^2_bO_x$, and (ii) at
- 35 least 1, 2, 3, 4 or 5 or more chemo/electro-active material that comprises $M^1_aM^2_bM^3_cO_x$.

Chemo/electro-active materials useful in the apparatus of this invention may be selected from one or more members of the group consisting of

- a chemo/electro-active material that
5 comprises $\text{Al}_a\text{Ni}_b\text{O}_x$
- a chemo/electro-active material that
comprises CeO_2 ,
- a chemo/electro-active material that
comprises $\text{Cr}_a\text{Mn}_b\text{O}_x$,
- 10 a chemo/electro-active material that
comprises $\text{Cr}_a\text{Ti}_b\text{O}_x$
- a chemo/electro-active material that
comprises $\text{Cr}_a\text{Y}_b\text{O}_x$
- a chemo/electro-active material that
15 comprises $\text{Cu}_a\text{Ga}_b\text{O}_x$,
- a chemo/electro-active material that
comprises $\text{Cu}_a\text{La}_b\text{O}_x$
- a chemo/electro-active material that
comprises CuO ,
- 20 a chemo/electro-active material that
comprises $\text{Fe}_a\text{La}_b\text{O}_x$
- a chemo/electro-active material that
comprises $\text{Fe}_a\text{Ni}_b\text{O}_x$
- a chemo/electro-active material that
25 comprises $\text{Fe}_a\text{Ti}_b\text{O}_x$
- a chemo/electro-active material that
comprises $\text{Ga}_a\text{Ti}_b\text{Zn}_c\text{O}_x$
- a chemo/electro-active material that
comprises $\text{Mn}_a\text{Ti}_b\text{O}_x$
- 30 a chemo/electro-active material that
comprises $\text{Nd}_a\text{Sr}_b\text{O}_x$,
- a chemo/electro-active material that
comprises $\text{Nb}_a\text{Ti}_b\text{O}_x$
- a chemo/electro-active material that
35 comprises $\text{Nb}_a\text{Ti}_b\text{Zn}_c\text{O}_x$
- a chemo/electro-active material that
comprises $\text{Nb}_a\text{W}_b\text{O}_x$

a chemo/electro-active material that
 comprises NiO,
 a chemo/electro-active material that
 comprises $\text{Ni}_a\text{Zn}_b\text{O}_x$
 5 a chemo/electro-active material that
 comprises Pr_6O_{11} ,
 a chemo/electro-active material that
 comprises $\text{Sb}_a\text{Sn}_b\text{O}_x$.
 a chemo/electro-active material that
 10 comprises SnO_2 ,
 a chemo/electro-active material that
 comprises $\text{Ta}_a\text{Ti}_b\text{O}_x$, and
 a chemo/electro-active material that
 comprises $\text{Ti}_a\text{Zn}_b\text{O}_x$.
 15 a chemo/electro-active material that
 comprises WO_3 , and
 a chemo/electro-active material that
 comprises ZnO.
 wherein a, b and c are each independently about 0.0005
 20 to about 1; and wherein x is a number sufficient so
 that the oxygen present balances the charges of the
 other elements in the chemo/electro-active material.

For the following materials, preferred ranges
 25 for a, b and c are approximately as follows:
 for $\text{Al}_a\text{Ni}_b\text{O}_x$, a = 0.005 to 0.25 and b = 0.75
 to 0.995;
 for $\text{Cr}_a\text{Mn}_b\text{O}_x$, a = 0.4 to 0.6 and b = 0.4 to
 0.6;
 30 for $\text{Cr}_a\text{Ti}_b\text{O}_x$, a = 0.985 to 0.9925 and b =
 0.0075 to 0.025, or a = 0.025 to 0.075 and b =
 0.925 to 0.975;
 for $\text{Cr}_a\text{Y}_b\text{O}_x$, a = 0.4 to 0.6 and b = 0.4 to 0.6;
 for $\text{Cu}_a\text{Ga}_b\text{O}_x$, a = 0.4 to 0.6 and b = 0.4 to
 35 0.6;
 for $\text{Cu}_a\text{La}_b\text{O}_x$, a = 0.15 to 0.45 and b = 0.55 to
 0.85;

for $\text{Fe}_a\text{La}_b\text{O}_x$, $a = 0.965$ to 0.995 and $b = 0.005$
 to 0.035 ;
 for $\text{Fe}_a\text{Ni}_b\text{O}_x$, $a = 0.55$ to 0.85 and $b = 0.15$ to
 0.45 ;
 5 for $\text{Fe}_a\text{Ti}_b\text{O}_x$, $a = 0.4$ to 0.6 and $b = 0.4$ to
 0.6 ;
 for $\text{Ga}_a\text{Ti}_b\text{Zn}_c\text{O}_x$, $a = 0.005$ to 0.015 , $b = 0.1$ to
 0.3 and $c = 0.65$ to 0.95 ;
 for $\text{Mn}_a\text{Ti}_b\text{O}_x$, $a = 0.4$ to 0.6 and $b = 0.4$ to
 10 0.6 ;
 for $\text{Nd}_a\text{Sr}_b\text{O}_x$, $a = 0.925$ to 0.975 and $b = 0.025$
 to 0.075 ;
 for $\text{Nb}_a\text{Ti}_b\text{O}_x$, $a = 0.005$ to 0.15 and $b = 0.85$
 to 0.995 ;
 15 for $\text{Nb}_a\text{Ti}_b\text{Zn}_c\text{O}_x$, $a = 0.005$ to 0.015 , $b = 0.1$ to
 0.3 and $c = 0.65$ to 0.95 ;
 for $\text{Nb}_a\text{W}_b\text{O}_x$, $a = 0.925$ to 0.975 and $b = 0.025$
 to 0.075 ;
 for $\text{Ni}_a\text{Zn}_b\text{O}_x$, $a = 0.4$ to 0.97 and $b = 0.03$ to
 20 0.6 ;
 for $\text{Sb}_a\text{Sn}_b\text{O}_x$, $a = 0.025$ to 0.075 and $b =$
 0.925 to 0.975 ;
 for $\text{Ta}_a\text{Ti}_b\text{O}_x$, $a = 0.005$ to 0.15 and $b = 0.85$
 to 0.995 ; and
 25 for $\text{Ti}_a\text{Zn}_b\text{O}_x$, $a = 0.085$ to 0.175 and $b = 0.825$
 to 0.915 .

Chemo/electro-active materials useful in this
 invention may also be selected from subgroups of the
 30 foregoing formed by omitting any one or more members
 from the whole group as set forth in the lists above.
 As a result, the chemo/electro-active materials may in
 such instance not only be any one or more member(s)
 selected from any subgroup of any size that may be
 35 formed from the whole group as set forth in the lists
 above, but the subgroup may also exclude the members
 that have been omitted from the whole group to form the
 subgroup. The subgroup formed by omitting various

members from the whole group in the lists above may, moreover, contain any number of the members of the whole group such that those members of the whole group that are excluded to form the subgroup are absent from the subgroup. Representative subgroups are set forth below.

Chemo/electro-active materials that comprise M^1O_x may, for example, be selected from the group consisting of

- a chemo/electro-active material that comprises CeO_2 ,
- a chemo/electro-active material that comprises CuO ,
- a chemo/electro-active material that comprises NiO ,
- a chemo/electro-active material that comprises Pr_6O_{11} ,
- a chemo/electro-active material that comprises SnO_2 ,
- a chemo/electro-active material that comprises WO_3 , and
- a chemo/electro-active material that comprises ZnO .

Of the above, one or more members of the group consisting of

- a chemo/electro-active material that comprises CeO_2 ,
- a chemo/electro-active material that comprises SnO_2 , and
- a chemo/electro-active material that comprises ZnO

may contain a frit additive, although when desired other materials that comprise M^1O_x may also contain a frit additive.

A chemo/electro-active material that comprises $M^1_a M^2_b O_x$, or a chemo/electro-active material that comprises $M^1_a M^2_b M^3_c O_x$, may be selected from the group consisting of

- 5 a chemo/electro-active material that comprises $Al_a Ni_b O_x$
- a chemo/electro-active material that comprises $Cr_a Mn_b O_x$,
- a chemo/electro-active material that
- 10 comprises $Cr_a Ti_b O_x$
- a chemo/electro-active material that comprises $Cr_a Y_b O_x$
- a chemo/electro-active material that comprises $Cu_a Ga_b O_x$,
- 15 a chemo/electro-active material that comprises $Cu_a La_b O_x$
- a chemo/electro-active material that comprises $Fe_a La_b O_x$
- a chemo/electro-active material that
- 20 comprises $Fe_a Ni_b O_x$
- a chemo/electro-active material that comprises $Fe_a Ti_b O_x$
- a chemo/electro-active material that comprises $Ga_a Ti_b Zn_c O_x$
- 25 a chemo/electro-active material that comprises $Mn_a Ti_b O_x$
- a chemo/electro-active material that comprises $Nd_a Sr_b O_x$,
- a chemo/electro-active material that
- 30 comprises $Nb_a Ti_b O_x$
- a chemo/electro-active material that comprises $Nb_a Ti_b Zn_c O_x$
- a chemo/electro-active material that comprises $Nb_a W_b O_x$
- 35 a chemo/electro-active material that comprises $Ni_a Zn_b O_x$
- a chemo/electro-active material that comprises $Sb_a Sn_b O_x$.

a chemo/electro-active material that
comprises $Ta_aTi_bO_x$, and
a chemo/electro-active material that
comprises $Ti_aZn_bO_x$.

5

Of the above, one or more members of the group
consisting of

a chemo/electro-active material that
comprises $Al_aNi_bO_x$

10

a chemo/electro-active material that
comprises $Cr_aTi_bO_x$

a chemo/electro-active material that
comprises $Cu_aLa_bO_x$

15

a chemo/electro-active material that
comprises $Fe_aLa_bO_x$

a chemo/electro-active material that
comprises $Fe_aNi_bO_x$

a chemo/electro-active material that
comprises $Fe_aTi_bO_x$

20

a chemo/electro-active material that
comprises $Ga_aTi_bZn_cO_x$

a chemo/electro-active material that
comprises $Nb_aTi_bO_x$

25

a chemo/electro-active material that
comprises $Nb_aTi_bZn_cO_x$

a chemo/electro-active material that
comprises $Nb_aW_bO_x$

a chemo/electro-active material that
comprises $Ni_aZn_bO_x$

30

a chemo/electro-active material that
comprises $Sb_aSn_bO_x$

a chemo/electro-active material that
comprises $Ta_aTi_bO_x$, and

35

a chemo/electro-active material that
comprises $Ti_aZn_bO_x$

may contain a frit additive, although when desired
other materials that comprise $M^1_aM^2_bO_x$, or that comprise
 $M^1_aM^2_bM^3_cO_x$, may also contain a frit additive.

In the apparatus of this invention, a chemo/electro-active material that comprises $M^1_a M^2_b O_x$ may be selected from one or more or all of the members
5 of the group consisting of

- a chemo/electro-active material that comprises $Al_a Ni_b O_x$
- a chemo/electro-active material that comprises $Cr_a Ti_b O_x$, and
- 10 a chemo/electro-active material that comprises $Fe_a La_b O_x$.

or one or more or all of the members of the group consisting of

- 15 a chemo/electro-active material that comprises $Cr_a Ti_b O_x$
- a chemo/electro-active material that comprises $Fe_a La_b O_x$, and
- a chemo/electro-active material that
- 20 comprises $Fe_a Ni_b O_x$

or one or more or all of the members of the group consisting of

- a chemo/electro-active material that
- 25 comprises $Fe_a La_b O_x$
- a chemo/electro-active material that comprises $Fe_a Ni_b O_x$, and
- a chemo/electro-active material that
- comprises $Ni_a Zn_b O_x$

30

or one or more or all of the members of the group consisting of

- a chemo/electro-active material that comprises $Fe_a Ni_b O_x$
- 35 a chemo/electro-active material that comprises $Ni_a Zn_b O_x$, and
- a chemo/electro-active material that comprises $Sb_a Sn_b O_x$.

or one or more or all of the members of the group consisting of

- a chemo/electro-active material that
- 5 comprises $\text{Al}_a\text{Ni}_b\text{O}_x$
- a chemo/electro-active material that
- comprises $\text{Cr}_a\text{Ti}_b\text{O}_x$
- a chemo/electro-active material that
- comprises $\text{Fe}_a\text{La}_b\text{O}_x$
- 10 a chemo/electro-active material that
- comprises $\text{Fe}_a\text{Ni}_b\text{O}_x$
- a chemo/electro-active material that
- comprises $\text{Ni}_a\text{Zn}_b\text{O}_x$, and
- a chemo/electro-active material that
- 15 comprises $\text{Sb}_a\text{Sn}_b\text{O}_x$.

or one or more or all of the members of the group consisting of

- a chemo/electro-active material that
- 20 comprises $\text{Al}_a\text{Ni}_b\text{O}_x$
- a chemo/electro-active material that
- comprises $\text{Cr}_a\text{Ti}_b\text{O}_x$, and
- a chemo/electro-active material that
- comprises $\text{Mn}_a\text{Ti}_b\text{O}_x$

25

or one or more or all of the members of the group consisting of

- a chemo/electro-active material that
- comprises $\text{Nb}_a\text{Ti}_b\text{O}_x$
- 30 a chemo/electro-active material that
- comprises $\text{Ni}_a\text{Zn}_b\text{O}_x$, and
- a chemo/electro-active material that
- comprises $\text{Sb}_a\text{Sn}_b\text{O}_x$

35 or one or more or all of the members of the group consisting of

- a chemo/electro-active material that
- comprises $\text{Ni}_a\text{Zn}_b\text{O}_x$

a chemo/electro-active material that
comprises $Sb_aSn_bO_x$, and
a chemo/electro-active material that
comprises $Ta_aTi_bO_x$

5

or one or more or all of the members of the group
consisting of

a chemo/electro-active material that
comprises $Sb_aSn_bO_x$

10

a chemo/electro-active material that
comprises $Ta_aTi_bO_x$, and

a chemo/electro-active material that
comprises $Ti_aZn_bO_x$.

15

or one or more or all of the members of the group
consisting of

a chemo/electro-active material that comprises
 $Cr_aMn_bO_x$

20

a chemo/electro-active material that comprises
 $Cr_aTi_bO_x$, and

a chemo/electro-active material that comprises
 $Cr_aY_bO_x$

25

or one or more or all of the members of the group
consisting of

a chemo/electro-active material that comprises
 $Cr_aTi_bO_x$

a chemo/electro-active material that comprises
 $Cr_aY_bO_x$, and

30

a chemo/electro-active material that comprises
 $Cu_aGa_bO_x$

or one or more or all of the members of the group
consisting of

35

a chemo/electro-active material that comprises
 $Cr_aY_bO_x$

a chemo/electro-active material that comprises
 $Cu_aGa_bO_x$, and

a chemo/electro-active material that comprises
 $\text{Cu}_a\text{La}_b\text{O}_x$

or one or more or all of the members of the group
5 consisting of

a chemo/electro-active material that comprises
 $\text{Cu}_a\text{Ga}_b\text{O}_x$

a chemo/electro-active material that comprises
 $\text{Cu}_a\text{La}_b\text{O}_x$, and

10 a chemo/electro-active material that comprises
 $\text{Fe}_a\text{La}_b\text{O}_x$.

or one or more or all of the members of the group
consisting of

15 a chemo/electro-active material that comprises
 $\text{Cr}_a\text{Mn}_b\text{O}_x$

a chemo/electro-active material that comprises
 $\text{Cr}_a\text{Ti}_b\text{O}_x$

20 a chemo/electro-active material that comprises
 $\text{Cr}_a\text{Y}_b\text{O}_x$

a chemo/electro-active material that comprises
 $\text{Cu}_a\text{Ga}_b\text{O}_x$

a chemo/electro-active material that comprises
 $\text{Cu}_a\text{La}_b\text{O}_x$, and

25 a chemo/electro-active material that comprises
 $\text{Fe}_a\text{La}_b\text{O}_x$.

or one or more or all of the members of the group
consisting of

30 a chemo/electro-active material that
comprises $\text{Cr}_a\text{Y}_b\text{O}_x$

a chemo/electro-active material that
comprises $\text{Cu}_a\text{Ga}_b\text{O}_x$, , and

35 a chemo/electro-active material that
comprises $\text{Cu}_a\text{La}_b\text{O}_x$

or one or more or all of the members of the group
consisting of

a chemo/electro-active material that
comprises $\text{Cu}_a\text{Ga}_b\text{O}_x$,

a chemo/electro-active material that
comprises $\text{Cu}_a\text{La}_b\text{O}_x$, and

5 a chemo/electro-active material that
comprises $\text{Fe}_a\text{Ti}_b\text{O}_x$

or one or more or all of the members of the group
consisting of

10 a chemo/electro-active material that comprises
 $\text{Cr}_a\text{Mn}_b\text{O}_x$

a chemo/electro-active material that comprises
 $\text{Mn}_a\text{Ti}_b\text{O}_x$, and

a chemo/electro-active material that comprises
15 $\text{Nd}_a\text{Sr}_b\text{O}_x$

In the apparatus of this invention, a
chemo/electro-active material that comprises $\text{M}^1_a\text{M}^2_b\text{O}_x$,
or a chemo/electro-active material that comprises
20 $\text{M}^1_a\text{M}^2_b\text{M}^3_c\text{O}_x$, may be selected from one or more or all of
the members of the group consisting of

a chemo/electro-active material that
comprises $\text{Cr}_a\text{Ti}_b\text{O}_x$

a chemo/electro-active material that
25 comprises $\text{Mn}_a\text{Ti}_b\text{O}_x$, and

a chemo/electro-active material that
comprises $\text{Nb}_a\text{Ti}_b\text{Zn}_c\text{O}_x$

or one or more or all of the members of the group
30 consisting of

a chemo/electro-active material that
comprises $\text{Mn}_a\text{Ti}_b\text{O}_x$

a chemo/electro-active material that
comprises $\text{Nb}_a\text{Ti}_b\text{Zn}_c\text{O}_x$, and

35 a chemo/electro-active material that
comprises $\text{Ta}_a\text{Ti}_b\text{O}_x$

or one or more or all of the members of the group consisting of

a chemo/electro-active material that comprises $\text{Nb}_a\text{Ti}_b\text{Zn}_c\text{O}_x$

5 a chemo/electro-active material that comprises $\text{Ta}_a\text{Ti}_b\text{O}_x$, and

a chemo/electro-active material that comprises $\text{Ti}_a\text{Zn}_b\text{O}_x$.

10 or one or more or all of the members of the group consisting of

a chemo/electro-active material that comprises $\text{Al}_a\text{Ni}_b\text{O}_x$

15 a chemo/electro-active material that comprises $\text{Cr}_a\text{Ti}_b\text{O}_x$

a chemo/electro-active material that comprises $\text{Mn}_a\text{Ti}_b\text{O}_x$

a chemo/electro-active material that comprises $\text{Nb}_a\text{Ti}_b\text{Zn}_c\text{O}_x$

20 a chemo/electro-active material that comprises $\text{Ta}_a\text{Ti}_b\text{O}_x$, and

a chemo/electro-active material that comprises $\text{Ti}_a\text{Zn}_b\text{O}_x$.

25 or one or more or all of the members of the group consisting of

a chemo/electro-active material that comprises $\text{Ga}_a\text{Ti}_b\text{Zn}_c\text{O}_x$

30 a chemo/electro-active material that comprises $\text{Nb}_a\text{Ti}_b\text{O}_x$, and

a chemo/electro-active material that comprises $\text{Ni}_a\text{Zn}_b\text{O}_x$

35 or one or more or all of the members of the group consisting of

a chemo/electro-active material that comprises $\text{Ga}_a\text{Ti}_b\text{Zn}_c\text{O}_x$

a chemo/electro-active material that
 comprises $Nb_aTi_bO_x$
 a chemo/electro-active material that
 comprises $Ni_aZn_bO_x$
 5 a chemo/electro-active material that
 comprises $Sb_aSn_bO_x$
 a chemo/electro-active material that
 comprises $Ta_aTi_bO_x$, and
 a chemo/electro-active material that
 10 comprises $Ti_aZn_bO_x$.

or one or more or all of the members of the group
 consisting of
 a chemo/electro-active material that
 15 comprises $Cu_aLa_bO_x$
 a chemo/electro-active material that
 comprises $Fe_aTi_bO_x$, and
 a chemo/electro-active material that
 comprises $Ga_aTi_bZn_cO_x$
 20

or one or more or all of the members of the group
 consisting of
 a chemo/electro-active material that
 comprises $Fe_aTi_bO_x$
 25 a chemo/electro-active material that
 comprises $Ga_aTi_bZn_cO_x$, and
 a chemo/electro-active material that
 comprises $Nb_aW_bO_x$.

30 or one or more or all of the members of the group
 consisting of
 a chemo/electro-active material that
 comprises $Cr_aY_bO_x$
 a chemo/electro-active material that
 35 comprises $Cu_aGa_bO_x$,
 a chemo/electro-active material that
 comprises $Cu_aLa_bO_x$

a chemo/electro-active material that
comprises $\text{Fe}_a\text{Ti}_b\text{O}_x$

a chemo/electro-active material that
comprises $\text{Ga}_a\text{Ti}_b\text{Zn}_c\text{O}_x$, and

5 a chemo/electro-active material that
comprises $\text{Nb}_a\text{W}_b\text{O}_x$.

or one or more or all of the members of the group
consisting of

10 a chemo/electro-active material that comprises
 $\text{Mn}_a\text{Ti}_b\text{O}_x$

a chemo/electro-active material that comprises
 $\text{Nd}_a\text{Sr}_b\text{O}_x$, and

a chemo/electro-active material that comprises
15 $\text{Nb}_a\text{Ti}_b\text{Zn}_c\text{O}_x$

In the apparatus of this invention, a
chemo/electro-active material that comprises M^1O_x , a
chemo/electro-active material that comprises $\text{M}^1_a\text{M}^2_b\text{O}_x$,
20 or a chemo/electro-active material that comprises
 $\text{M}^1_a\text{M}^2_b\text{M}^3_c\text{O}_x$, may be selected from one or more or all of
the members of the group consisting of

a chemo/electro-active material that
comprises $\text{Ga}_a\text{Ti}_b\text{Zn}_c\text{O}_x$

25 a chemo/electro-active material that
comprises $\text{Nb}_a\text{Ti}_b\text{O}_x$

a chemo/electro-active material that
comprises $\text{Ni}_a\text{Zn}_b\text{O}_x$, and

a chemo/electro-active material that comprises
30 SnO_2

or one or more or all of the members of the group
consisting of

35 a chemo/electro-active material that
comprises $\text{Ga}_a\text{Ti}_b\text{Zn}_c\text{O}_x$

a chemo/electro-active material that
comprises $\text{Nb}_a\text{Ti}_b\text{O}_x$

- a chemo/electro-active material that comprises $\text{Ni}_a\text{Zn}_b\text{O}_x$
 - a chemo/electro-active material that comprises SnO_2 ,
 - 5 a chemo/electro-active material that comprises $\text{Ta}_a\text{Ti}_b\text{O}_x$, and
 - a chemo/electro-active material that comprises $\text{Ti}_a\text{Zn}_b\text{O}_x$.
- 10 or one or more or all of the members of the group consisting of
 - a chemo/electro-active material that comprises $\text{Nd}_a\text{Sr}_b\text{O}_x$
 - a chemo/electro-active material that comprises
 - 15 $\text{Nb}_a\text{Ti}_b\text{Zn}_c\text{O}_x$, and
 - a chemo/electro-active material that comprises Pr_6O_{11}
- or one or more or all of the members of the group
 - 20 consisting of
 - a chemo/electro-active material that comprises $\text{Nb}_a\text{Ti}_b\text{Zn}_c\text{O}_x$
 - a chemo/electro-active material that comprises Pr_6O_{11} , and
 - 25 a chemo/electro-active material that comprises $\text{Ti}_a\text{Zn}_b\text{O}_x$.
- or one or more or all of the members of the group
 - consisting of
 - 30 a chemo/electro-active material that comprises $\text{Cr}_a\text{Mn}_b\text{O}_x$
 - a chemo/electro-active material that comprises $\text{Mn}_a\text{Ti}_b\text{O}_x$
 - a chemo/electro-active material that comprises
 - 35 $\text{Nd}_a\text{Sr}_b\text{O}_x$
 - a chemo/electro-active material that comprises $\text{Nb}_a\text{Ti}_b\text{Zn}_c\text{O}_x$

a chemo/electro-active material that comprises Pr_6O_{11} , and
a chemo/electro-active material that comprises $\text{Ti}_a\text{Zn}_b\text{O}_x$.

5

In the apparatus of this invention, a chemo/electro-active material that comprises M^1O_x , or a chemo/electro-active material that comprises $\text{M}^1_a\text{M}^2_b\text{O}_x$ may be selected from one or more or all of the members
10 of the group consisting of

a chemo/electro-active material that comprises $\text{Nb}_a\text{Ti}_b\text{O}_x$

a chemo/electro-active material that comprises $\text{Ni}_a\text{Zn}_b\text{O}_x$, and

15 a chemo/electro-active material that comprises SnO_2 .

or one or more or all of the members of the group consisting of

20 a chemo/electro-active material that comprises $\text{Ni}_a\text{Zn}_b\text{O}_x$

a chemo/electro-active material that comprises SnO_2 , and

25 a chemo/electro-active material that comprises $\text{Ta}_a\text{Ti}_b\text{O}_x$

or one or more or all of the members of the group consisting of

30 a chemo/electro-active material that comprises SnO_2 ,

a chemo/electro-active material that comprises $\text{Ta}_a\text{Ti}_b\text{O}_x$, and

a chemo/electro-active material that comprises $\text{Ti}_a\text{Zn}_b\text{O}_x$.

35

or one or more or all of the members of the group consisting of

- a chemo/electro-active material that comprises $Nb_aTi_bO_x$
 - a chemo/electro-active material that comprises $Ni_aZn_bO_x$
 - 5 a chemo/electro-active material that comprises $Sb_aSn_bO_x$, and
 - a chemo/electro-active material that comprises ZnO.
- 10 or one or more or all of the members of the group consisting of
 - a chemo/electro-active material that comprises $Ni_aZn_bO_x$
 - a chemo/electro-active material that
 - 15 comprises $Sb_aSn_bO_x$
 - a chemo/electro-active material that comprises $Ta_aTi_bO_x$, and
 - a chemo/electro-active material that comprises ZnO
- 20 or one or more or all of the members of the group consisting of
 - a chemo/electro-active material that comprises $Sb_aSn_bO_x$
 - 25 a chemo/electro-active material that comprises $Ta_aTi_bO_x$
 - a chemo/electro-active material that comprises $Ti_aZn_bO_x$, and
 - a chemo/electro-active material that comprises
 - 30 ZnO
- or one or more or all of the members of the group consisting of
 - a chemo/electro-active material that
 - 35 comprises $Ta_aTi_bO_x$
 - a chemo/electro-active material that comprises $Ti_aZn_bO_x$, and

a chemo/electro-active material that comprises
ZnO.

or one or more or all of the members of the group
5 consisting of

a chemo/electro-active material that
comprises $Nb_aTi_bO_x$

a chemo/electro-active material that
comprises $Ni_aZn_bO_x$

10 a chemo/electro-active material that
comprises $Sb_aSn_bO_x$

a chemo/electro-active material that
comprises $Ta_aTi_bO_x$

15 a chemo/electro-active material that
comprises $Ti_aZn_bO_x$, and

a chemo/electro-active material that
comprises ZnO.

or one or more or all of the members of the group
20 consisting of

a chemo/electro-active material that comprises
 $Al_aNi_bO_x$

a chemo/electro-active material that comprises
 $Cr_aMn_bO_x$, and

25 a chemo/electro-active material that comprises
CuO

or one or more or all of the members of the group
consisting of

30 a chemo/electro-active material that comprises
 $Cr_aMn_bO_x$

a chemo/electro-active material that comprises
CuO, and

35 a chemo/electro-active material that comprises
 $Nd_aSr_bO_x$

or one or more or all of the members of group
consisting of

a chemo/electro-active material that comprises
CuO

a chemo/electro-active material that comprises
 $\text{Nd}_a\text{Sr}_b\text{O}_x$, and

5 a chemo/electro-active material that comprises
 Pr_6O_{11}

or one or more or all of the members of group
consisting of

10 a chemo/electro-active material that comprises
 $\text{Nd}_a\text{Sr}_b\text{O}_x$

a chemo/electro-active material that comprises
 Pr_6O_{11} , and

15 a chemo/electro-active material that comprises
 WO_3 .

or one or more or all of the members of group
consisting of

20 a chemo/electro-active material that comprises
 $\text{Al}_a\text{Ni}_b\text{O}_x$

a chemo/electro-active material that comprises
 $\text{Cr}_a\text{Mn}_b\text{O}_x$

a chemo/electro-active material that comprises
CuO

25 a chemo/electro-active material that comprises
 $\text{Nd}_a\text{Sr}_b\text{O}_x$

a chemo/electro-active material that comprises
 Pr_6O_{11} , and

30 a chemo/electro-active material that comprises
 WO_3 .

To form a chemo/electro-active material that
is $\text{M}^1_a\text{M}^2_b\text{O}_x$ or $\text{M}^1_a\text{M}^2_b\text{M}^3_c\text{O}_x$, component metal oxides may be
mixed in powder form with n-propanol, sieved to a fine
35 mesh and ball milled, roll milled or prepared as a
paste using a Mueller glass plate mixer. Any method
of depositing the chemo/electro-active material to a
substrate is suitable. One technique used for

deposition is applying a semiconducting material on an alumina substrate on which electrodes are screen printed. The semiconducting material can be deposited on top of electrodes by hand painting semiconducting materials onto the substrate, pipetting materials into wells, thin film deposition, or thick film printing techniques. Most techniques are followed by calcining and a final firing at 850~1050°C to sinter the semiconducting materials.

10

Techniques for screen-printing substrates with the electrodes and chemo/electro-active materials are illustrated in Figures 2-3. Figure 2 depicts a method of using interdigitated electrodes overlaid with dielectric material, forming blank wells into which the chemo/electro-active materials can be deposited.

15

Figure 3 depicts an electrode screen pattern for an array of 6 materials, which is printed on both sides of the substrate to provide for a 12-material array chip.

20

Two of the electrodes are in parallel so it holds only 6 unique materials. Counting down from the top of the array shown in Fig. 3, the top two materials can only be accessed simultaneously by the split electrode with which they have shared contact. Below that is the

25

screen pattern for the dielectric material, which is screen printed on top of the electrodes on both sides of the substrate to prevent the material from being fouled by contact with the gas mixture, such as a deposit of soot that could reduce the sensitivity of a

30

sensor material to a gas or cause a short. Below that is the screen pattern for the actual sensor materials. This is printed in the holes in the dielectric on top of the electrodes. When more than one material is used in the array, the individual materials are printed one at a time.

35

The geometry of a sensor material as fabricated in an array, including such characteristics

as its thickness, selection of a compound or composition for use as the sensor, and the voltage applied across the array, can vary depending on the sensitivity required. If desired, the apparatus may be constructed in a size such that it may be passed through an opening that is the size of a circle having a diameter of no more than about 150 mm, or no more than about 100 mm, or no more than about 50 mm, or no more than about 25 mm, or no more than about 18 mm, as the requirements of its usage may dictate. The sensor materials are preferably connected in parallel in a circuit to which a voltage of about 1 to about 20, preferably about 1 to about 12, volts is applied across the sensor materials.

As noted, the types of electrical response characteristics that may be measured include AC impedance or resistance, capacitance, voltage, current or DC resistance. It is preferred to use resistance as the electric response characteristic of a sensor material that is measured to perform analysis of a gas mixture and/or a component therein. For example, a suitable sensor material may be that which, when at a temperature of about 400°C or above, has a resistivity of at least about 1 ohm-cm, and preferably at least about 10 ohm-cm, and yet no more than about 10^6 ohm-cm, preferably no more than about 10^5 ohm-cm, and more preferably no more than about 10^4 ohm-cm. Such a sensor material may also be characterized as that which exhibits, preferably at a temperature of about 400°C or above, upon exposure to a gas mixture, a change in resistance of at least about 0.1 percent, and preferably at least about 1 percent, as compared to the resistance in the absence of exposure.

Regardless of the type of response characteristic that is measured for the purpose of analyzing a mixture and/or a gaseous component of

interest therein, it is desirable that a sensor material be utilized for which a quantified value of that response characteristic is stable over an extended period of time. When the sensor material is exposed to
5 a mixture containing the analyte, the concentration of the analyte being a function of the composition of the particular gas mixture in which it is contained, the value of the response of the sensor material will preferably remain constant or vary to only a small
10 extent during exposure to the mixture over an extended period of time at a constant temperature. For example, the value of the response, if it varies, will vary by no more than about twenty percent, preferably no more than about ten percent, more preferably no more than
15 about five percent, and most preferably no more than about one percent over a period of at least about 1 minute, or preferably a period of hours such as at least about 1 hour, preferably at least about 10 hours, more preferably at least about 100 hours, and most
20 preferably at least about 1000 hours. One of the advantages of the types of sensor materials described above is that they are characterized by this kind of stability of response.

25 An electrical response is determined for each chemo/electro-active material upon exposure of the array to a gas mixture, and means for determining the response include conductors interconnecting the sensor materials. The conductors are in turn connected to
30 electrical input and output circuitry, including data acquisition and manipulation devices as appropriate to measure and record a response exhibited by a sensor material in the form of an electrical signal. The value of a response, such as a measurement related to
35 resistance, may be indicated by the size of the signal. One or more signals may be generated by an array of sensors as to each analyte component in the mixture,

whether the analyte is one or more individual gases and/or one or more subgroups of gases.

An electrical response is determined for each individual chemo/electro-active material separately from that of each of the other chemo/electro-active materials. This can be accomplished by accessing each chemo/electro-active material with an electric current sequentially, using a multiplexer to provide signals differentiated between one material and another in, for example, the time domain or frequency domain. It is consequently preferred that no chemo/electro-active material be joined in a series circuit with any other such material. One electrode, by which a current is passed to a chemo/electro-active material, can nevertheless be laid out to have contact with more than one material. An electrode may have contact with all, or fewer than all, of the chemo/electro-active materials in an array. For example, if an array has 12 chemo/electro-active materials, an electrode may have contact with each member of a group of 2, 3, 4, 5 or 6 (or, optionally, more in each instance) of the chemo/electro-active materials. The electrode will preferably be laid out to permit an electrical current to be passed to each member of such group of chemo/electro-active materials sequentially.

A conductor such as a printed circuit may be used to connect a voltage source to a sensor material, and, when a voltage is applied across the sensor material, a corresponding current is created through the material. Although the voltage may be AC or DC, the magnitude of the voltage will typically be held constant. The resulting current is proportional to both the applied voltage and the resistance of the sensor material. A response of the material in the form of either the current, voltage or resistance may be determined, and means for doing so include

commercial analog circuit components such as precision resistors, filtering capacitors and operational amplifiers (such as a OPA4340). As voltage, current and resistance is each a known function of the other
5 two electrical properties, a known quantity for one property may be readily converted to that of another.

Resistance may be determined, for example, in connection with the digitization of an electrical
10 response. Means for digitizing an electrical response include an analog to digital (A/D) converter, as known in the art, and may include, for example, electrical components and circuitry that involve the operation of a comparator. An electrical response in the form of a
15 voltage signal, derived as described above as a result of applying a voltage across a sensor material, is used as an input to a comparator section (such as a LM339). The other input to the comparator is driven by a linear ramp produced by charging a capacitor using a constant
20 current source configured from an operational amplifier (such as a LT1014) and an external transistor (such as a PN2007a). The ramp is controlled and monitored by a microcomputer (such as a T89C51CC01). A second comparator section is also driven by the ramp voltage,
25 but is compared to a precise reference voltage. The microcomputer captures the length of time from the start of the ramp to the activation of the comparators to generate a signal based on the counted time.

30 The resistance of the sensor material is then calculated, or quantified as a value, by the microcomputer from the ratio of the time signal derived from the voltage output of the material to a time signal corresponding to a known look-up voltage and,
35 ultimately, to the resistance that is a function of the look-up voltage. A microprocessor chip, such as a T89C51CC01, can be used for this function. The microprocessor chip may also serve as means for

determining a change in the resistance of a sensor material by comparing a resistance, determined as above, to a previously determined value of the resistance.

5

Electrical properties such as impedance or capacitance may be determined, for example, by the use of circuitry components such as an impedance meter, a capacitance meter or inductance meter.

10

Means for digitizing the temperature of an array of chemo/electro-active materials can include, for example, components as described above that convert a signal representative of a physical property, state or condition of a temperature measuring device to a signal based on counted time.

In one embodiment, analysis of a multi-component gas mixture is complete upon the generation of an electrical response, such as resistance, in the manner described above. As a measurement of resistance exhibited by a sensor material upon exposure to a gas mixture is a function of the partial pressure within the mixture of one or more component gases, the measured resistance provides useful information about the composition of the gas mixture. The information may, for example, indicate the presence or absence within the mixture of a particular gas or subgroup of gases. In other embodiments, however, it may be preferred to manipulate, or further manipulate, an electrical response in the manner necessary to obtain information related to the concentration within the mixture of one or more particular component gases or subgroups of gases, or to calculate the actual concentration within the mixture of one or more component gases or subgroups.

Means for obtaining a determination of or information concerning the relative concentration within the mixture of one or more individual component gases and/or one or more subgroups of gases, or
5 concerning the detected presence of, or calculating the actual concentration of, one or more individual component gases and/or subgroups within the mixture, may include a modeling algorithm that incorporates either a PLS (Projection onto Latent Systems) model, a
10 back-propagation neural network model, or a combination of the two, along with signal pre-processing and output post-processing. Signal pre-processing includes, but is not limited to, such operations as principle component analyses, simple linear transformations and
15 scaling, logarithmic and natural logarithmic transformations, differences of raw signal values (e.g., resistances), and differences of logarithmic values. The algorithm contains a model whose parameters have been previously determined, and that
20 empirically models the relationship between the pre-processed input signal and information related to the gas concentration of the species of interest. Output post-processing includes, but is not limited to, all of the operations listed above, as well as their inverse
25 operations.

The model is constructed using equations in which constants, coefficients or other factors are derived from pre-determined values characteristic of a
30 precisely measured electrical response of an individual sensor material to a particular individual gas or subgroup expected to be present as a component in the mixture to be analyzed. The equations may be constructed in any manner that takes temperature into
35 account as a value separate and apart from the electrical responses exhibited by the sensor materials upon exposure to a gas mixture. Each individual sensor material in the array differs from each of the

other sensors in its response to at least one of the component gases or subgroups in the mixture, and these different responses of each of the sensors is determined and used to construct the equations used in
5 the model.

A change of temperature in the array may be indicated by a change in the quantified value of an electrical response characteristic, resistance for
10 example, of a sensor material. At a constant partial pressure in the mixture of a gas of interest, the value of an electrical response characteristic of a sensor material may vary with a change in temperature of the array, and thus the material. This change in the value
15 of an electrical response characteristic may be measured for the purpose of determining or measuring the extent of change of, and thus a value for, temperature. It is not required, but is preferred, that this measurement of temperature be made
20 independently of information related to the compositional content of a gas mixture. This can be done by not using sensors that provide compositional information for the additional purpose of determining temperature, and, optionally, by connecting the
25 temperature measuring device in parallel circuitry with the sensor materials, rather than in series. Means for measuring temperature include a thermocouple or a pyrometer incorporated with an array of sensors. If the temperature determining device is a thermistor, which
30 is typically a material that is not responsive to an analyte gas, the thermistor is preferably made from a different material than the material from which any of the gas sensors is made. Regardless of the method by which temperature or change in temperature is
35 determined, a temperature value or a quantified change in temperature of the array is a desirable input, preferably in digitized form, from which an analysis of

a mixture of gases and/or a component therein may be performed.

In the method and apparatus of this invention, unlike various prior-art technologies, there is no need to separate the component gases of a mixture for purposes of performing an analysis, such as by a membrane or electrolytic cell. There is also no need when performing an analysis by means of this invention to employ a reference gas, such as for the purpose of bringing a response or analytical results back to a base line value, or adjusting a response or analytical results in terms of a reference state. With the exception of preliminary testing, during which a standardized response value to be assigned to the exposure of each individual sensor material to each individual analyte gas is determined, the sensor materials are exposed only to the mixture in which an analyte gas and/or subgroup is contained. The sensor materials are not exposed to any other gas to obtain response values for comparison to those obtained from exposure to the mixture containing an analyte. The analysis of the mixture is therefore performed in continuous mode only from the electrical responses obtained upon exposure of the chemo/electro-active materials to the mixture containing the analyte. No information about an analyte gas and/or subgroup is inferred by exposure of the sensor materials to any gas other than the analyte itself as contained within the mixture. A determination related to the presence or concentration of a component in the gas mixture may therefore be obtained from no information about the gas mixture other than the individual electrical response of the chemo/electro-active materials in an array.

This invention is therefore useful at the higher temperatures found in automotive emission systems, typically in the range of from about 400°C to

about 1000°C. In addition to gasoline and diesel internal combustion engines, however, there is a variety of other combustion processes to which this invention could be applied, including stack or burner emissions of all kinds such as resulting from chemical manufacturing, electrical generation, waste incineration and air heating. These applications require the detection of gases such as nitrogen oxides, ammonia, carbon monoxide, hydrocarbons and oxygen at the ppm to per cent levels, typically in a highly corrosive environment.

When the multi-component gas mixture comprises any or all of a nitrogen oxide, a hydrocarbon, ammonia, or any of the other gases mentioned herein, the apparatus may be used to determine the presence and/or concentration of a nitrogen oxide, ammonia and/or a hydrocarbon in the multi-component gas mixture. The apparatus may also be used to determine the presence and/or concentration of any one or more of the other gases mentioned herein that may be present in a multi-component gas mixture. For this purpose, the electrical response, in the apparatus of this invention, of one or more of a chemo/electro-active material that comprises M^1O_x , a chemo/electro-active material that comprises $M^1_a M^2_b O_x$, and a chemo/electro-active material that comprises $M^1_a M^2_b M^3_c O_x$, may be related to one or more of the presence of a nitrogen oxide within the gas mixture, the presence of ammonia within the gas mixture, the presence of a hydrocarbon within the gas mixture, the collective concentration of all nitrogen oxides within the gas mixture, the concentration of ammonia within the gas mixture, and/or the concentration of a hydrocarbon within the gas mixture. The electrical response, in the apparatus of this invention, of one or more of chemo/electro-active materials is also capable of distinguishing between the presence and/or concentration of a nitrogen oxide and

ammonia, and may be used to determine lambda, which is the air/fuel ratio in a combustion exhaust, or may be combined with a separate lambda sensor.

5 This invention is also useful for detecting and measuring gases in other systems such as those in which odor detection is important, and/or that are at lower temperature, such as in the medical, agricultural or food and beverage industries, or in the ventilation
10 system of a building or a vehicle for transportation. An array of chemo/electro-active materials could be used, for example, to supplement the results of, or calibrate, a gas chromatograph.

15 This invention therefore provides methods and apparatus for directly sensing the presence and/or concentration of one or more gases in an multi-component gas system, comprising an array of at least two chemo/electro-active materials chosen to detect
20 analyte gases or subgroups of gases in a multi-component gas stream. The multi-component gas system can be at essentially any temperature that is not so low or so high that the sensor materials are degraded or the sensor apparatus otherwise malfunctions. In one
25 embodiment, the gas system may be at a lower temperature such as room temperature (about 25°C) or elsewhere in the range of about 0°C to less than about 100°C, whereas in other embodiments the gas mixture may at a higher temperature such as in the range of about
30 400°C to about 1000°C or more. The gas mixture may therefore have a temperature that is about 0°C or more, about 100°C or more, about 200°C or more, about 300°C or more, about 400°C or more, about 500°C or more, about 600°C or more, about 700°C or more, or about
35 800°C or more, and yet is less than about 1000°C, is less than about 900°C, is less than about 800°C, is less than about 700°C, is less than about 600°C, is less than about 500°C, is less than about 400°C, is

less than about 300°C, is less than about 200°C, or is less than about 100°C.

5 In applications in which the gas mixture is above about 400°C, the temperature of the sensor materials and the array is a result of substantially only, and preferably is a result of solely, the temperature of the gas mixture in which a gaseous analyst is contained. This is typically a variable
10 temperature. When higher-temperature gases are being analyzed, it may be desirable to provide a heater with the array to bring the sensor materials quickly to a minimum temperature. Once the analysis has begun, however, the heater (if used) is typically switched
15 off, and no method is provided to maintain the sensor materials at a preselected temperature. The temperature of the sensor materials thus rises or falls to the same extent that the temperature of the surrounding environment does. The temperature of the
20 surrounding environment, and thus the sensors and the array, is typically a result of substantially only the temperature of the gas mixture to which the array is exposed.

25 In applications in which the gas mixture is below about 400°C, it may be preferred to maintain the sensor materials and the array at a preselected temperature of about 200°C or above, and preferably 400°C or above. This preselected temperature may be
30 substantially constant, or preferably is constant. The preselected temperature may also be about 500°C or above, about 600°C or above, about 700°C or above, about 800°C or above, about 900°C or above, or about 1000°C or above. This may be conveniently done with a
35 heater incorporated with the array, in a manner as known in the art. If desired, a separate micro heater means may be supplied for each separate chemo/electro-active material, and any one or more of the materials

may be heated to the same or a different temperature. The temperature of the gas mixture in such case may also be below about 300°C, below about 200°C, below about 100°C, or below about 50°C. In these low
5 temperature applications, the means for heating the chemo/electro-active materials may be a voltage source that has a voltage in the range of about 10^{-3} to about 10^{-6} volts. The substrate on which the materials are placed may be made of a material that is selected from
10 one or more of the group consisting of silicon, silicon carbide, silicon nitride, and alumina containing a resistive dopant. Devices used in these low temperature applications are often small enough to be held in the human hand.

15
This heating technique is also applicable, however, to the analysis of high temperature gases. When the temperature of the gas mixture is above about 400°C, the sensor materials may in alternative
20 embodiments be continually maintained by a heater at a minimum preselected temperature that may be higher than the temperature of the gas mixture. Such preselected temperature may be about 500°C or above, about 600°C or above, about 700°C or above, about 800°C or above,
25 about 900°C or above, or about 1000°C or above. In certain instances, although the temperature of the gas may be higher than this preselected temperature, a heater is nevertheless available to cycle on if needed to continually maintain the sensor materials at a
30 minimum of the preselected temperature.

The gas mixture to be analyzed may be emitted by a process, or may be a product of a chemical reaction that is transmitted to a device. In such
35 instance, the apparatus of this invention may further include means for utilizing the electrical response of an array, and optionally a temperature measurement, for the purpose of controlling the process or the device.

Means for utilizing an electrical response of a sensor material, and optionally a temperature measurement, for controlling a process or device include a decision making routine to control, for example, the chemical reaction of combustion that occurs in an internal combustion engine, or to control the engine itself, or components or equipment associated therewith.

10

Combustion is a process in which the chemical reaction of the oxidation of a hydrocarbon fuel occurs in the cylinder of an engine. An engine is a device to which a result of that chemical reaction is transmitted, the result being the force generated by the combustion reaction to the work necessary to move the piston in the cylinder. Another example of a process that emits a multi-component mixture of gases is the chemical reaction that occurs in a fuel cell, and other examples of a device to which a product of a chemical reaction is transmitted is a boiler, such as used in a furnace or for power generation, or a scrubber in a stack to which waste gases are transmitted for pollution abatement treatment.

25

In the case of an engine, to control the process of combustion or the operation of the engine itself, a microcomputer (such as a T89C51CC01) performs a multitude of decision-making routines about various parameters of the process of combustion or about operating characteristics of the engine. The microcomputer gathers information about the compositional content of the engine exhaust, and does so by obtaining the responses of an array of chemo/electro-active materials that have been exposed to the stream of exhaust, and optionally obtains a temperature measurement. The information is temporarily stored in a random access memory, and the

35

microcomputer then applies one or more decision-making routines to the information.

A decision-making routine utilizes one or
5 more algorithms and/or mathematical operations to
manipulate the acquired information to generate a
decision in the form of a value that is equivalent to a
desired state or condition that should be possessed by
a particular parameter of the process, or by an
10 operating characteristic of the device. Based on the
result of a decision-making routine, instructions are
given by or are controlled by the microcomputer that
cause an adjustment in the state or condition of a
parameter of the process or an operating characteristic
15 of the device. In the case of the process embodied by
the chemical reaction of combustion, the process can be
controlled by adjusting a parameter of the reaction,
such as the relative amount of the reactants fed
thereto. The flow of fuel or air to the cylinder, for
20 example, can be increased or decreased. In the case
of the engine itself, being a device to which a result
of the reaction of combustion is transmitted, control
can be accomplished by adjusting an operating
characteristic of the engine such as torque or engine
25 speed.

An internal combustion engine and the
associated components and equipment, controlled by the
methods and apparatus of this invention, can be used
30 for many different purposes including, for example, in
any type of vehicle for transportation or recreation
such as a car, truck, bus, locomotive, aircraft,
spacecraft, boat, jet ski, all-terrain vehicle or
snowmobile; or in equipment for construction,
35 maintenance or industrial operations such as pumps,
lifts, hoists, cranes, generators, or equipment for
demolition, earth moving, digging, drilling, mining or
groundskeeping.

In summary, it may be seen that this invention provides means to determine, measure and record responses exhibited by each of the chemo/electro-active materials present in an array upon exposure to a gas mixture. Any means that will determine, measure and record changes in electrical properties can be used, such as a device that is capable of measuring the change in AC impedance of the materials in response to the concentration of adsorbed gas molecules at their surfaces. Other means for determining electrical properties are suitable devices to measure, for example, capacitance, voltage, current or DC resistance. Alternatively a change in temperature of the sensing material may be measured and recorded. The chemical sensing method and apparatus may further provide means to measure or analyze a mixture and/or the detected gases such that the presence of the gases are identified and/or their concentrations are measured. These means can include instrumentation or equipment that is capable, for example, of performing chemometrics, neural networks or other pattern recognition techniques. The chemical sensor apparatus will further comprise a housing for the array of chemo/electro-active materials, the means for detecting, and means for analyzing.

The device includes a substrate, an array of at least two chemo/electro-active materials chosen to detect one or more predetermined gases in a multi-component gas stream, and a means to detect changes in electrical properties in each of the chemo/electro-active materials present upon exposure to the gas system. The array of sensor materials should be able to detect an analyte of interest despite competing reactions caused by the presence of the several other components of a multi-component mixture. For this

purpose, this invention uses an array or multiplicity of sensor materials, as described herein, each of which has a different sensitivity for at least one of the gas components of the mixture to be detected. A sensor
5 that has the needed sensitivity, and that can operate to generate the types of analytical measurements and results described above, is obtained by selection of appropriate compositions of materials from which the sensor is made. Various suitable types of materials
10 for this purpose are described above. The number of sensors in the array is typically greater than or equal to the number of individual gas components to be analyzed in the mixture.

15 Further description relevant to the apparatus of this invention, uses for the apparatus and methods of using the apparatus may be found in U.S. Provisional Application No. 60/370,445, filed April 5, 2002, and U.S. Application SN 10/117,472, filed April 5, 2002,
20 each of which is incorporated in its entirety as a part hereof for all purposes.

Where an apparatus or method of this invention is stated or described as comprising,
25 including, containing or having certain components or steps, it is to be understood, unless the statement or description explicitly provides to the contrary, that one or more components or steps other than those explicitly stated or described may be present in the
30 apparatus or method. In an alternative embodiment, however, the apparatus or method of this invention may be stated or described as consisting essentially of certain components or steps, in which embodiment components or steps that would materially alter the
35 principle of operation or the distinguishing characteristics of the apparatus or method would not be present therein. In a further alternative embodiment, the apparatus or method of this invention may be stated

or described as consisting of certain components or steps, in which embodiment components or steps other than those as stated would not be present therein.

5 Where the indefinite article "a" or "an" is used with respect to a statement or description of the presence of a component in an apparatus, or a step in a method, of this invention, it is to be understood, unless the statement or description explicitly provides
10 to the contrary, that the use of such indefinite article does not limit the presence of the component in the apparatus, or of the step in the method, to one in number.

15 The advantageous effects of this invention are demonstrated by the experimental work described below. The embodiments of the invention with which this experimental work is concerned are illustrative only, and do not limit the scope of the invention.

20 A variety of chemo/electro-active materials were tested to determine which of them displayed performance characteristics making them good candidates for selection as members of an array for use in an
25 apparatus for analyzing mixtures of gases. In a first screening evaluation, materials were exposed to the exhaust gas from a propane burner, and the resulting change in resistance of a circuit connected to each material was recorded. The increase or decrease in
30 resistance of each material as the material was exposed to the stream of exhaust gas over a period of time was recorded, and an algorithm was used to derive from the resistance readings a prediction of the presence and/or concentration of the various component gases in the gas
35 mixture generated as exhaust from combustion in the propane burner. The components of the exhaust gas stream were simultaneously measured with a slow chemiluminescent device ("CLD"), which enabled direct

comparison of predicted gas composition to measured gas composition. All of this data was subjected to principal component analysis, and the AC impedance of each material was also reviewed to verify that the material would be characterized by a stable frequency regime when exposed to a gas mixture.

In a second screening evaluation, chemo/electro-active materials that tend not to adhere well to an alumina substrate were mixed with frits. All materials, including those that were mixed with frits and those that were not, were then exposed to mixtures of synthetic gases in a pipe reactor. The synthetic gases from which the mixtures were made are NO₂, C₃H₈, O₂, and CO. The change in resistance of a circuit connected to each material resulting from exposure to the various gas mixtures was recorded. The increase or decrease in resistance of each material as the material was exposed to the gas mixture over a period of time was recorded, and an algorithm was used to derive from the resistance readings a prediction of the presence and/or concentration of the various component gases in the gas mixture. The components of the gas mixture were simultaneously measured with a slow CLD, which enabled direct comparison of predicted gas composition to measured gas composition. All of this data was subjected to principal component analysis, and the materials tested were also reviewed in terms of chemical considerations of material stability and adhesion.

These two screening evaluations produced a list of materials that were indicated to be good candidates for selection as members of an array in a gas analyzing apparatus of this invention. The materials may be described as metal oxides or mixtures of metal oxides, and are set forth in the lists below.

Metal Oxides

CeO₂

SnO₂

ZnO

CeO₂ with frit

SnO₂ with frit

ZnO with frit

NiO

5

Mixtures of Metal Oxides

(a) Oxide of	(b) Oxide of	(c) Oxide of	Molar ratio of (a) / (b) or (a) / (b) / (c)	Frit
Al	Ni		1/199	Yes
Cr	Ti		1/19	No
Cr	Ti		1/19	Yes
Cr	Y		1/1	No
Cu	La		1/2	Yes
Fe	La		40/1	No
Fe	La		40/1	Yes
Fe	Ni		2/1	No
Fe	Ni		2/1	Yes
Fe	Ti		1/1	No
Fe	Ti		1/1	Yes
Ga	Ti	Zn	1/19/80	No
Ga	Ti	Zn	1/19/80	Yes
Mn	Ti		1/1	No
Nb	Ti		1/19	No
Nb	Ti		1/19	Yes
Nb	Ti		1/99	No
Nb	Ti		1/99	Yes
Nb	Ti	Zn	1/19/80	No
Nb	Ti	Zn	1/19/80	Yes
Nb	W		19/1	No
Nb	W		19/1	Yes
Ni	Zn		1/1	No
Ni	Zn		1/1	Yes
Ni	Zn		2/1	No

Ni	Zn		2/1	Yes
Sb	Sn		1/19	Yes
Ta	Ti		1/24	No
Ta	Ti		1/24	Yes
Ta	Ti		1/99	No
Ta	Ti		1/99	Yes
Ti	Zn		3/22	No
Ti	Zn		3/22	Yes

The materials listed above were subjected to a 49-state evaluation by testing in a propane burner at temperatures of 370°C and 430°C. The 49 states in which the materials were tested were created by adding different mixtures of synthetic gases (e.g. NO₂, C₃H₈, O₂, and CO) to the exhaust of the propane burner to create a total of 49 different gas mixtures.

Individual metal oxides, or component metal oxides for incorporation into mixtures, for this test were purchased from a supplier such as Aldrich, Johnson Matthey, Fisher or Alfa. Each mixture of materials was formed from the component metal oxides in the molar ratio as indicated. Where a mixture of metal oxides was used, no attempt was made to determine if the material formed from the mixture had a single phase or had multiple phases. Where noted in the above list, frits were added at 10 volume percent to certain materials.

To form a mixture, the component metal oxides were mixed in powder form with n-propanol. Each material, whether an individual metal oxide or a mixture, and whether or not containing frits, was prepared for testing in a small batch (~20 grams), sieved to -325 mesh and ball milled prior to being calcined and fired at 1050°C. The majority of the materials were prepared as pastes using a Mueller glass

plate mixer, however two were roll milled as indicated by the notation "RM" in the list below.

Materials in the 49-state evaluation were exposed to the exhaust gas from a propane burner together with the synthetic gases, and the resulting change in resistance of a circuit connected to each material was recorded. The increase or decrease in resistance of each material as the material was exposed to the stream of exhaust gas over a period of time was recorded, and an algorithm was used to derive from the resistance readings a prediction of the presence and/or concentration of the various component gases in the gas mixture generated as exhaust from combustion in the propane burner. The components of the exhaust gas stream were simultaneously measured with a slow CLD, which enabled direct comparison of predicted gas composition to measured gas composition. All of this data was subjected to principal component analysis, and from the analysis the following sub-group was selected for further testing.

Metal Oxides

25 NiO SnO₂ with frit ZnO with frit

Mixtures of Metal Oxides

(a) Oxide of	(b) Oxide of	(c) Oxide of	Molar ratio of (a)/(b) or (a)/(b)/(c)	Frit
Al	Ni		1/199	Yes
Cr	Ti		1/19	Yes
Fe	La		40/1	Yes
Fe	Ni		2/1	Yes
Ga	Ti	Zn	1/19/80	No

Nb	Ti		1/19	No
Nb	Ti		1/19	Yes
Ni	Zn		1/1	Yes
Ni	Zn		2/1	Yes RM
Sb	Sn		1/19	Yes
Ti	Zn		3/22	Yes

The materials listed above, as selected from
 the 49-state evaluation, were subjected to a simulated
 5 service evaluation in which they were tested in a
 gasoline direct injection engine system. The
 materials were used in an apparatus that was exposed to
 the exhaust of the engine. The materials were
 prepared for the engine test in essentially the same
 10 manner as those tested in the 49-state evaluation
 except that the batch size was increased to 100 grams.
 In the engine evaluation, the materials were exposed to
 the exhaust gas of a lean burn engine having a NO_x
 storage catalyst. The testing consisted of running
 15 the engine at five different states of constant RPM and
 load. The substrate on which the materials were
 located was heated to a temperature of at least about
 480°C. The change in resistance of a circuit
 connected to each material resulting from exposure to
 20 the engine exhaust was recorded. The increase or
 decrease in resistance of each material as the material
 was exposed to the exhaust gas over the period of the
 test was recorded, and an algorithm involving a
 projection onto latent systems ("PLS") model was used
 25 to derive from the resistance readings a prediction of
 the concentration of NO_x in the stream of exhaust gas.
 The exhaust gas was simultaneously measured with a fast
 CLD, which enabled direct comparison of predicted NO_x
 concentration to the measured NO_x concentration. The
 30 root mean square error of the amount of NO_x determined

by the PLS model compared to the amount measured by the CLD is 19.5 ppm. The amount of each predicted determination of NOx concentration was plotted against the amount of the CLD measurement at the same time.

- 5 The plot of all measurements is shown in Figure 4, from which it may be seen that an array of chemo/electro-active materials may be used to determine the presence or concentration of components in a gas mixture within acceptable limits of error.

10